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Vij, Ashwani, "Matchmaking in Polynitrogen Chemistry: Search for Prospective Anions for
Combinations with N_5^+ "

(Statement A)

ACS National Meeting
(New Orleans, LA, 23-27 March 2003) (Deadline: **RUSH**, per RCC)

Matchmaking in Polynitrogen Chemistry: Search for prospective anions for combination with N_5^+



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Award Symposium for Karl Christe, March 25-26, 2003
225th National ACS Meeting, New Orleans



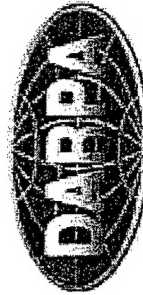
Coauthors & Project Sponsors



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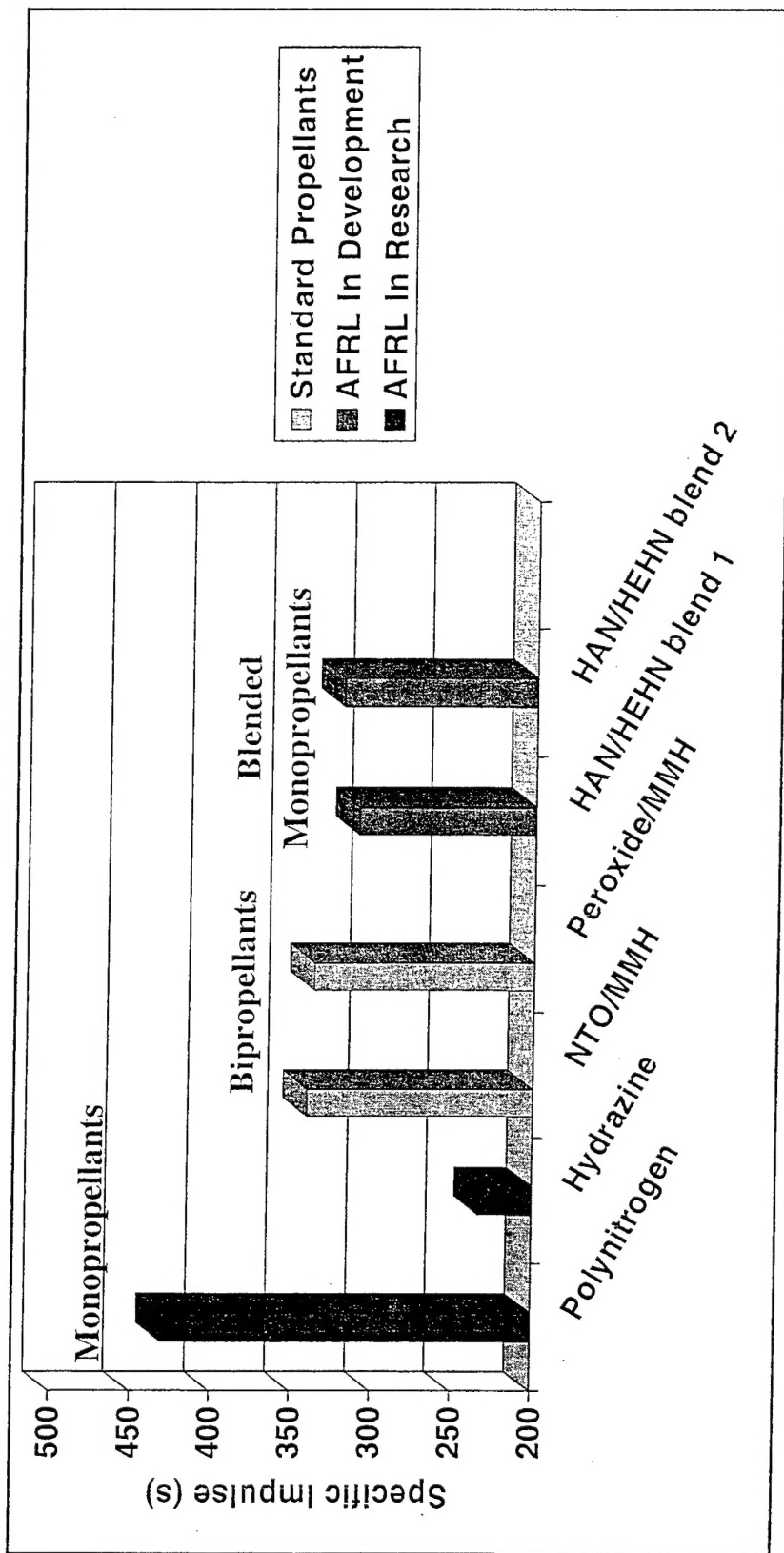
Why Polynitrogen Compounds ?



- Polynitrogen compounds contain only nitrogen atoms and are expected to have unusual properties. Most important among these are:
 - *High endothermicity*
 - *“Green” propellant*
- *“combustion” product is only gaseous N_2*
- *High density*
- *High I_{sp} values when compared to other monopropellants or bipropellants*
- *High detonation velocity*



Predicted Specific Impulse (s) Values for Neutral Polynitrogen Compounds





Synthesis and Properties of N_5^+

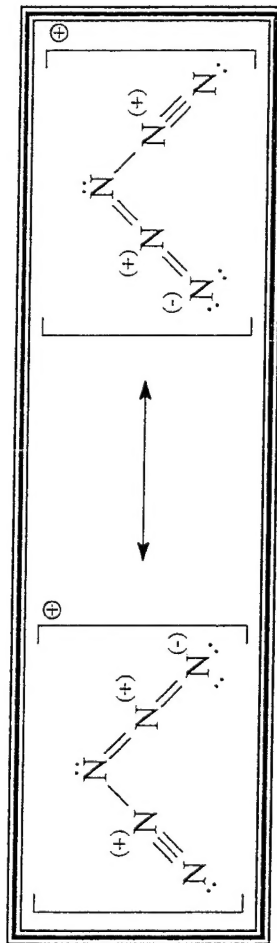
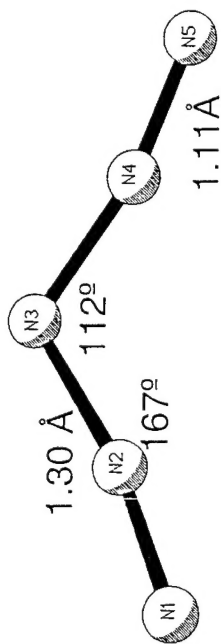


- First compound made was $N_5^+AsF_6^-$
 - ⇒ -78°C, 5 days, 60% purity, 50 mg scale
 - ⇒ Unstable at room temperature
 - ⇒ Exploded in low-temperature Raman spectrometer
- Second compound made was $N_5^+SbF_6^-$
$$N_2F^+SbF_6^- + HN_3 \longrightarrow N_5^+SbF_6^-$$
 - ⇒ First run: -64°C, 5 days, 80% purity, 300 mg scale
 - ⇒ Present method: Room temp., ½ day, 100% purity, 4 g scale

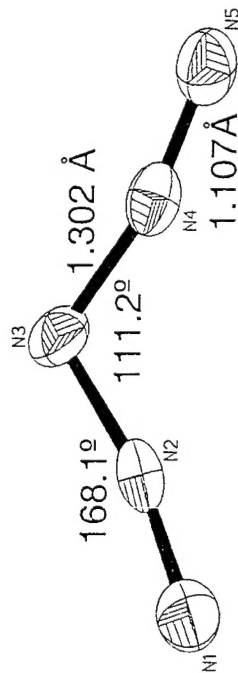
- Properties of $N_5^+SbF_6^-$:
 - ⇒ White solid
 - ⇒ Thermally stable to 70°C
 - ⇒ Survives impact sensitivity test (drop weight) at 150 kg/cm



Geometry of the N_5^+ Cation Predicted versus Experimental



Calculated Structure

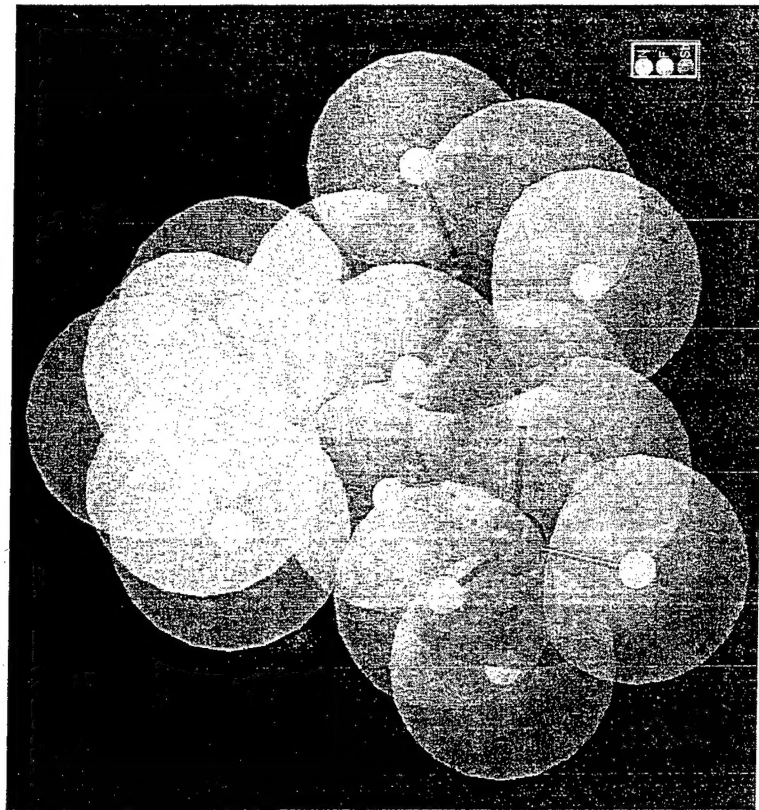


Experimental Structure

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Structure of the N_5^+ Cation



The Structure of $N_5^+Sb_2F_{11}^-$

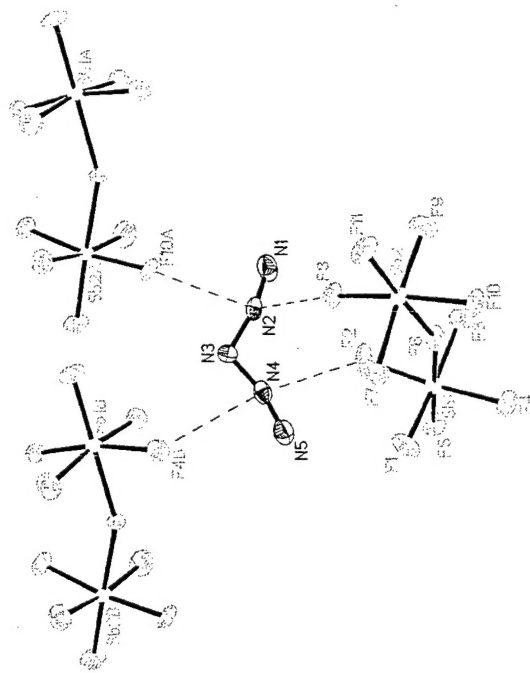
- ✓ The crystals grown from a mixture of SO_2 and SO_2ClF
- ✓ Crystal belong to the *Monoclinic* space group $C2/c$.
- ✓ Cell constants: $a = 10.913 \text{ \AA}$, $b = 12.654 \text{ \AA}$, $c = 16.675 \text{ \AA}$; $\beta = 104.72^\circ$
- ✓ $Z = 8$
- ✓ $R = 0.0678$

Inter-ionic Clipping!!

The N_5^+ cation fits into the $Sb_2F_{11}^-$ bend thus locking it, thereby precluding any possibilities of twisting



Crystal Packing Effects



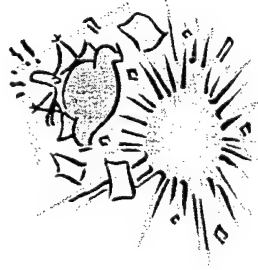
- ✓ The N...F Contacts support the resonance structure, where the N2 and N4 nitrogen atoms have a positive charge.
- ✓ N2 makes contacts at 2.723 and 2.768 Å; N4 contacts are at 2.887 and 2.814 Å



(In)Compatability of N_5^+



**Attempts to couple N_5^+ with energetic anions
can result in explosive reactions !!!**





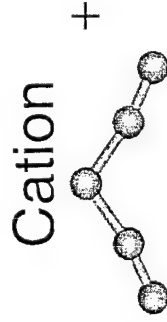
Recipe for Synthesizing Neutral Polynitrogen Compounds



- Combine a polynitrogen cation with a polynitrogen anion to form a neutral polynitrogen compound.



ONLY TWO STABLE POLYINITROGEN IONS KNOWN TO EXIST
IN BULK



N_5^+ cation

(discovered in 1999, AFRL, Christe)



N_3^- anion

(discovered in 1890, Curtius)

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What Determines the Stability of a Polynitrogen Species?



Stability of a Polynitrogen Salt is Determined by
Thermodynamic and Kinetic Factors

Thermodynamic Factors

1. Electron Affinity of the Cation
 - A fixed value, if we aim for a N_5^+ salt, i.e., 10.5-11.5 eV
2. First Ionization Potential of the Anion
 - The azide ion has a very low value of about 2.1 eV, which is the main reason for the instability of $N_5^+N_3^-$
 - New polynitrogen anions are needed with higher first IP values. **N_5^- and N_7^- anions are most promising candidates**



What Determines the Stability of a Neutral Polynitrogen Species?



3. Lattice Energy of the Crystal

- U_L fixed by the molar volumes of cation and anion. Born-Haber cycle calculations for the lattice energy estimated for $N_5^+N_3^-$ are 50 kcal/mole lower than the requirement for the stabilization of an ionic salt

Kinetic Factor

- Activation Energy Barriers of the Ions Towards Decomposition
 - These energy values determine the stability of the individual ions



Polynitrogen for Dummies I



What has Thermodynamics and Kinetics

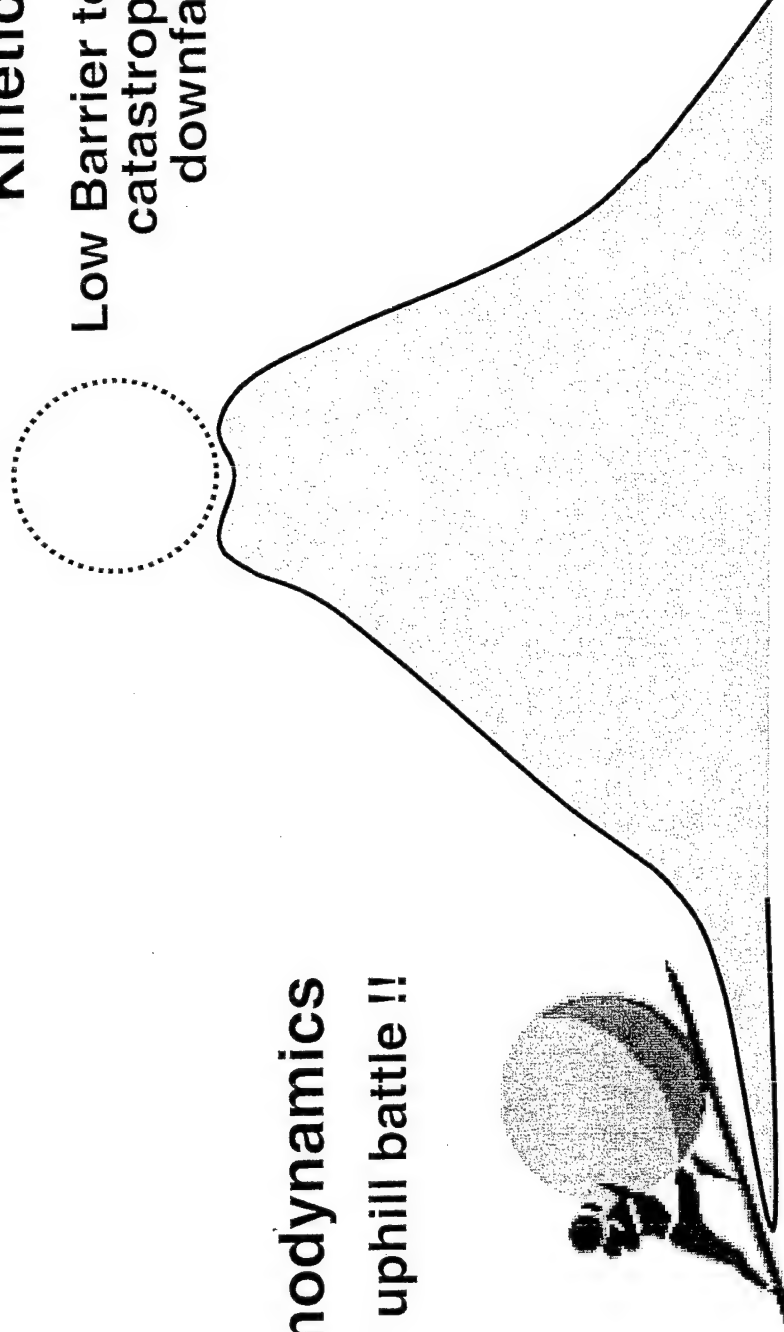
got to do with it ??

Kinetics

Low Barrier towards
catastrophic
downfall

Thermodynamics

It is an uphill battle !!

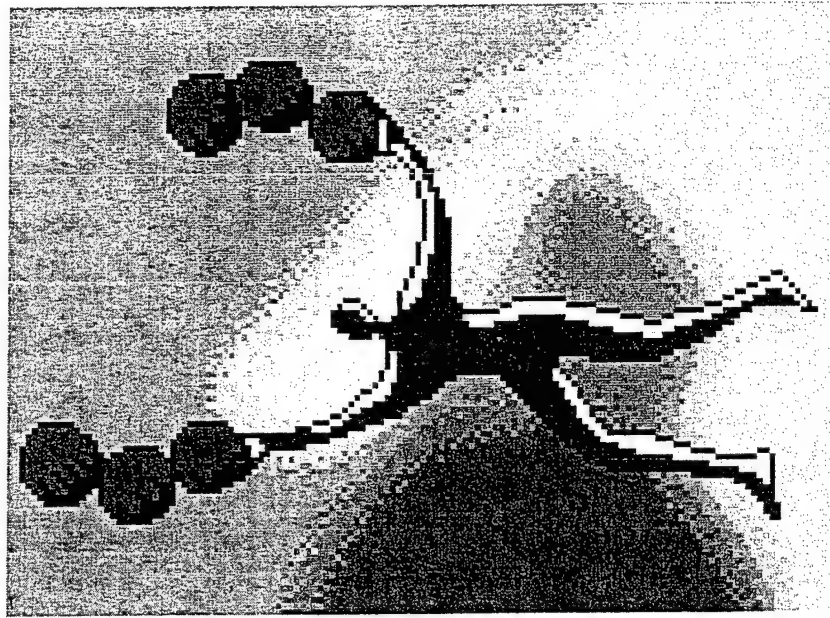




Polynitrogen for Dummies II



- Metastability requires a delicate balancing act !!



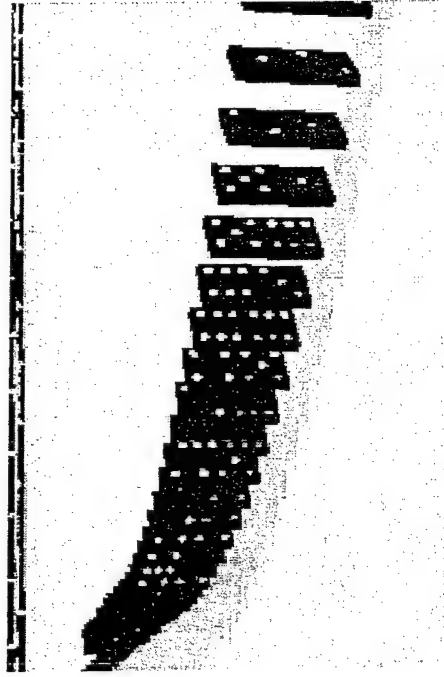
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Polynitrogen for *Dummies* III



Avoid a domino effect !!!

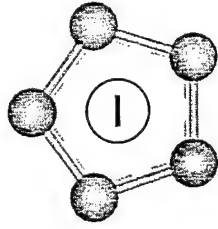


**Assembling a polynitrogen chain is like assembling metastable
dominos with perfect spacing, without prematurely triggering an
unwanted collapse**

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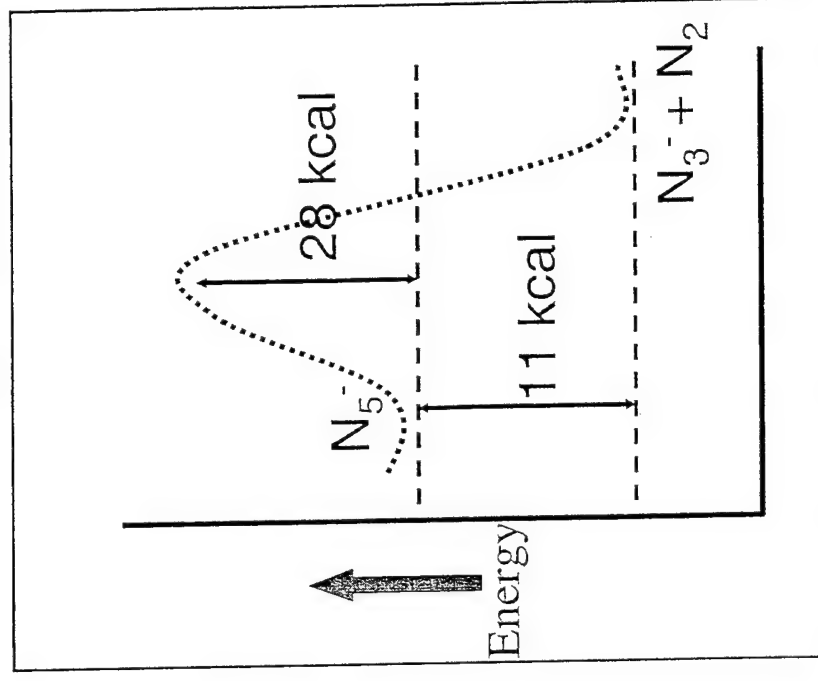


New Polynitrogen Anions as Counterparts for N_5^+



Pentazole anion (N_5^-)

- Theoretical calculations show that this anion has a 28 kcal/mole activation energy barrier for decomposition and its decomposition to N_3^- and N_2 is only 11 kcal/mol exothermic
- Aryl substituted pentazoles can be isolated as stable compounds only if stored at low temperatures. In methanol, these compounds rapidly decompose at room temperature to form aryl azides and N_2 gas



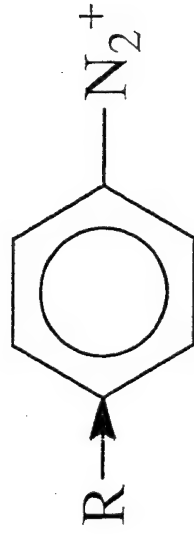
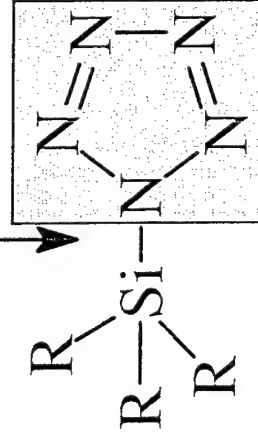
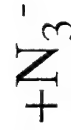
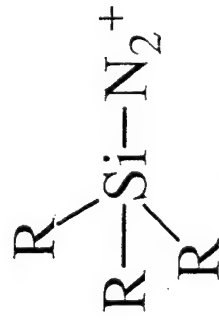
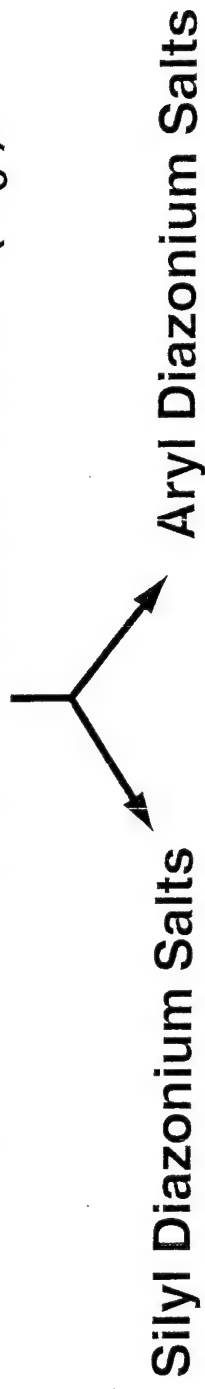


Synthetic Challenge – How do we make These New Anions??

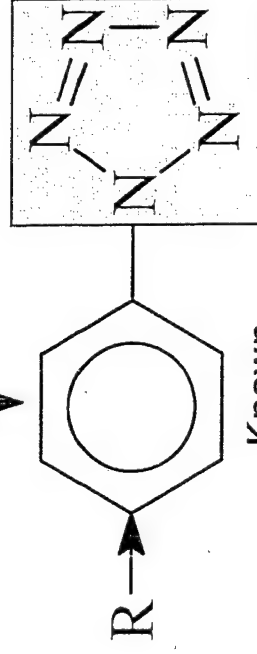
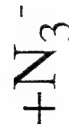


Synthesis of Substituted Pentazoles

Sources for the Pentazole Anion (N_5^-)



R = electron
releasing group



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Formation and Stability of Silyl Diazonium Salts



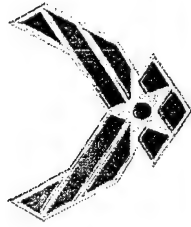
- Failed attempts to synthesize silyl diazonium salts



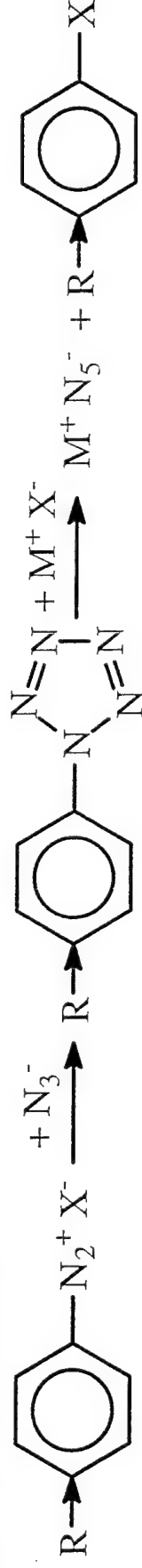
- R_3SiN_2^+ salts are unstable and spontaneously lose N_2



Theoretical calculations support this experimental observation

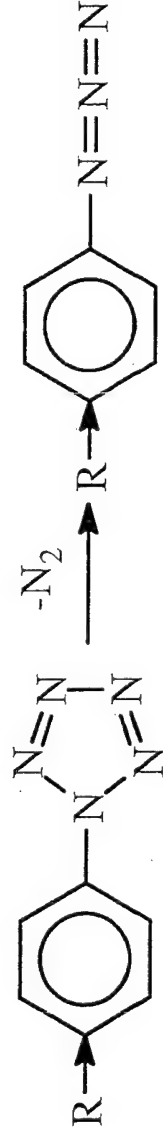


Use of Aryl Diazonium Salts – A Better Bet!



- R must be an electron releasing group, i.e., -NMe₂, -OH, -OCH₃, -OC₆H₅, -O⁻, etc.
- Some of these substituted arylpentazoles have been known for about four decades but **no success** had been achieved to cleave the N₅ ring from the aryl group

Aryl Pentazoles can rapidly lose N₂ at room temperature



I. Ugi, *Angew Chem.*, **1961**, 73, 172 and references therein

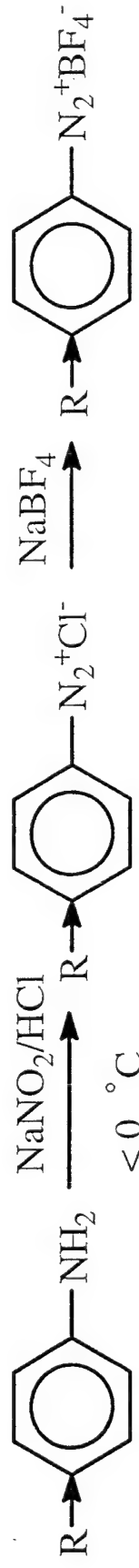
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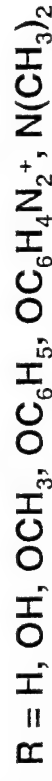
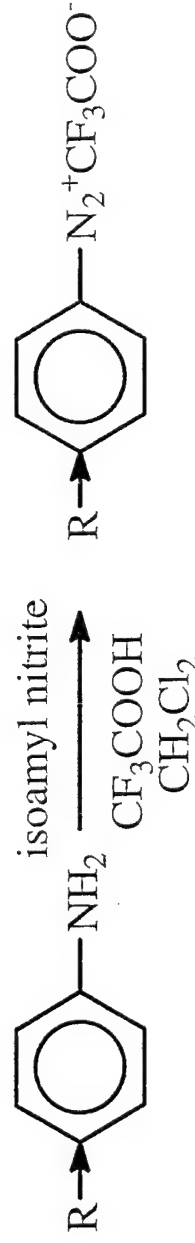
Synthesis of Aryldiazonium Salts



Aqueous Media



Non-aqueous Media

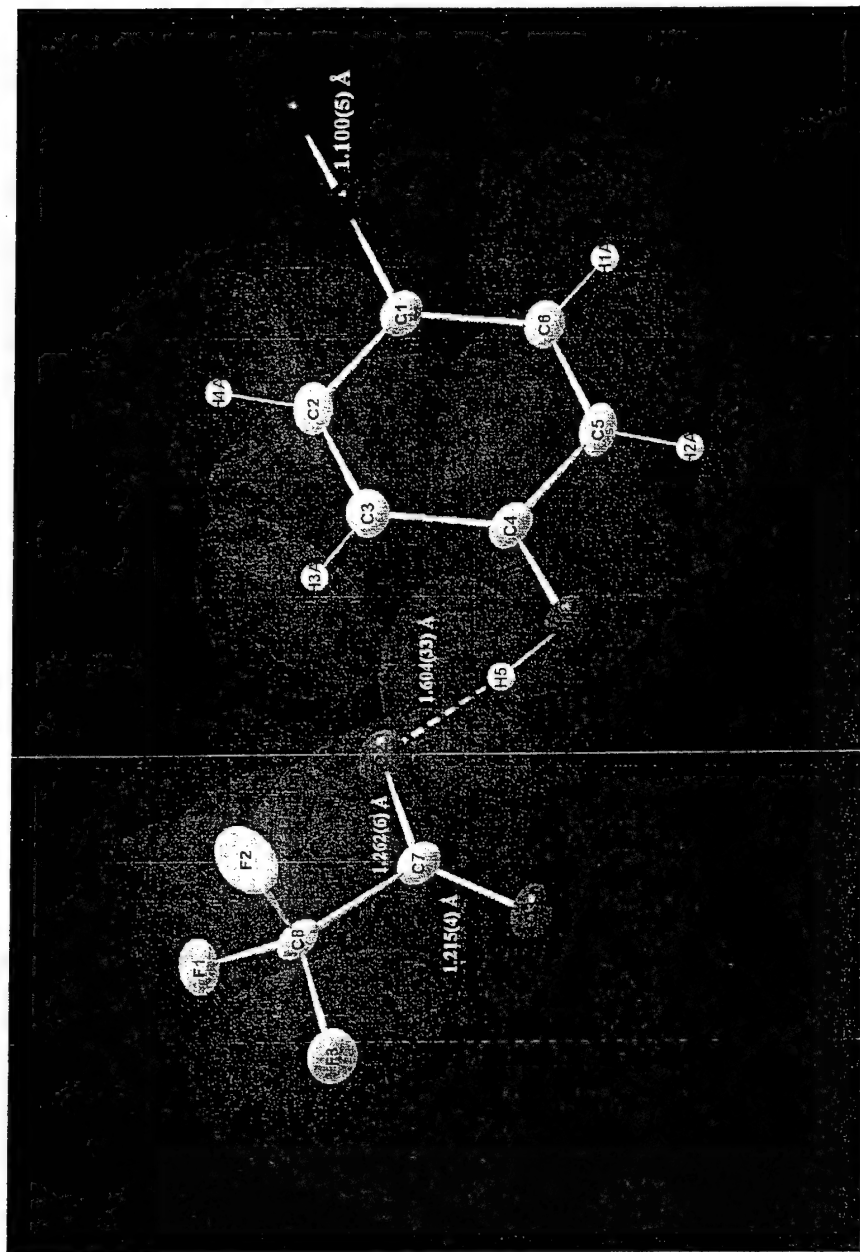
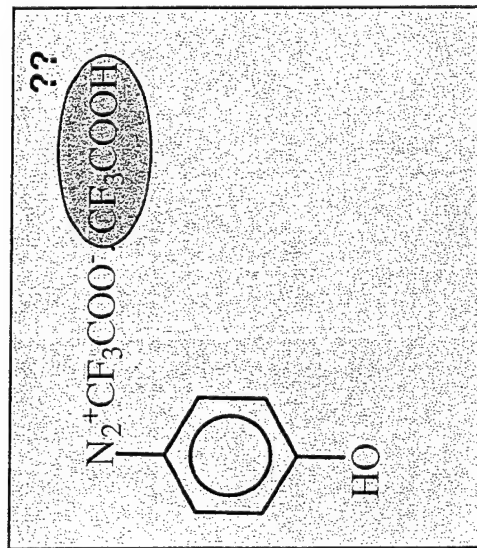




Single or Double Salt ?

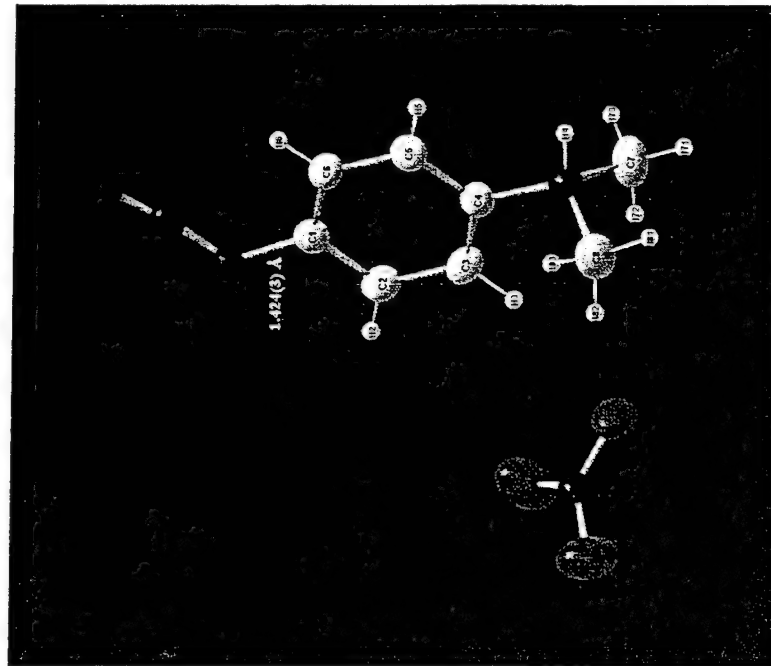
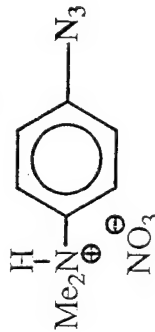
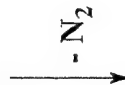
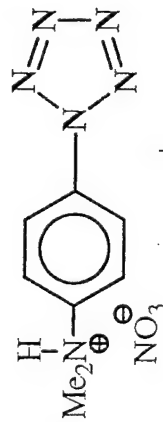
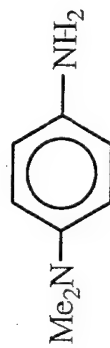


Colas and Goeldner, *Eur. J. Org. Chem.* **1999**, 1357-1366 reported the p-phenoxy diazonium salt to be a double salt. However, X-ray crystallography reveals no such stoichiometry.



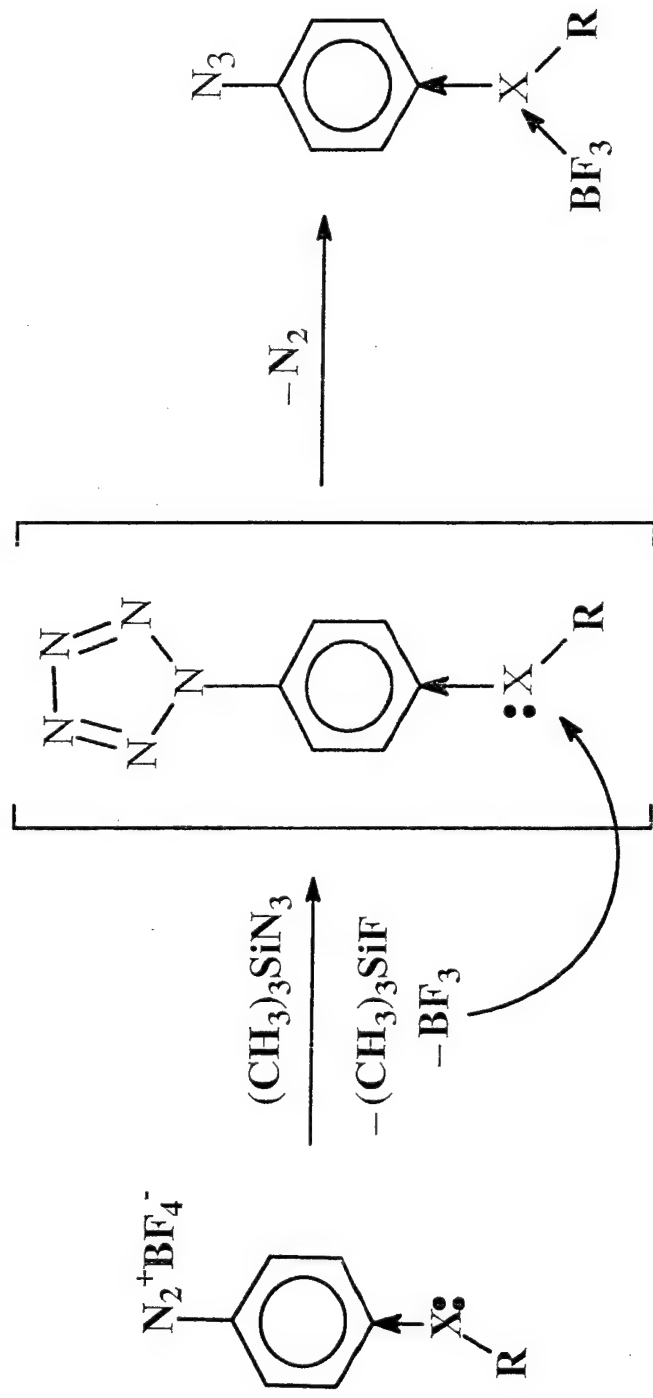
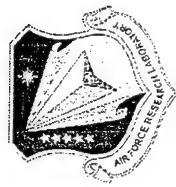


Role of the Lone Pair at Para Position





Reaction with Trimethylsilyl Azide



$\text{X} = \text{N}, \text{O}$

No pentazoles were isolated !!!

Reactions carried out in acetonitrile at -30°C

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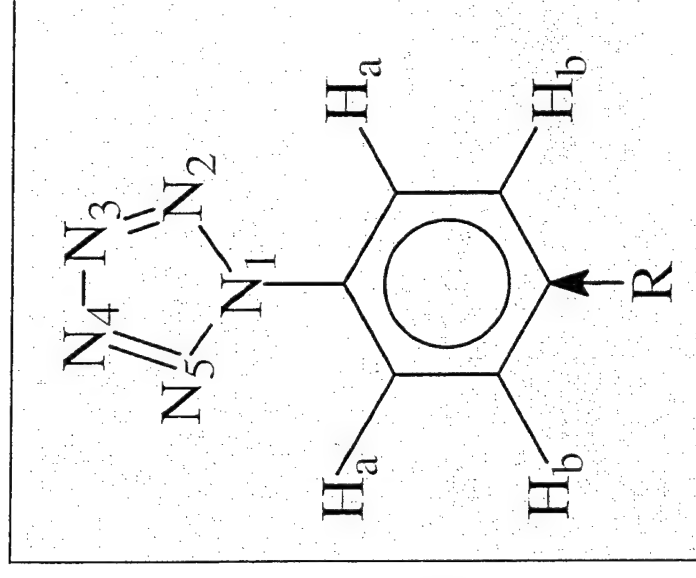


Identification of Arylpentazoles



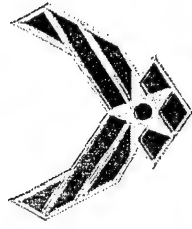
Pentazoles can be characterized by low temperature NMR spectral studies using ^{15}N labeled samples.

- ^1H NMR: AB-type spectrum with H_a and H_b at 8.0 and 7.0 ppm
- ^{14}N NMR: N_1 at ~ -80 ppm
- ^{15}N NMR: N_2/N_5 at ~ -27 ppm and N_3/N_4 at ~ -4 ppm



Note: Qualitative evidence for the presence of a pentazole ring: N_2 gas evolution in solution

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Cleavage of the Aryl-Pentazole Bond with Retention of the Pentazole Ring



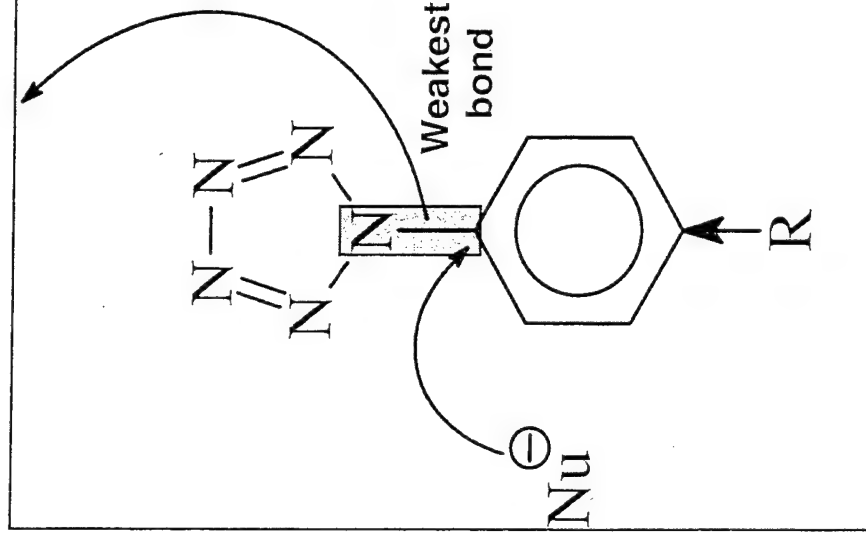
- **Chemical Methods**

- Ozonolysis does not work! (Ugi, Radziszewski)
V. Benin, P. Kszynski and G. J. Radziszewski, *J. Org. Chem.*, 2002, 67, 1354.

- Nucleophilic substitution using strong nucleophiles such as the OH⁻, OR⁻, F⁻ etc.

- **Collisional Fragmentation (ElectroSpray Ion Mass Spectroscopy – ESIMS)**

- Electrospray is very gentle and produces high concentration of the parent anion which can be mass selected
- Collisional fragmentation of the mass selected anions with variable collisional energies allow tailoring of fragmentation
- Negative ion detection eliminates interference from neutral or positively charged species

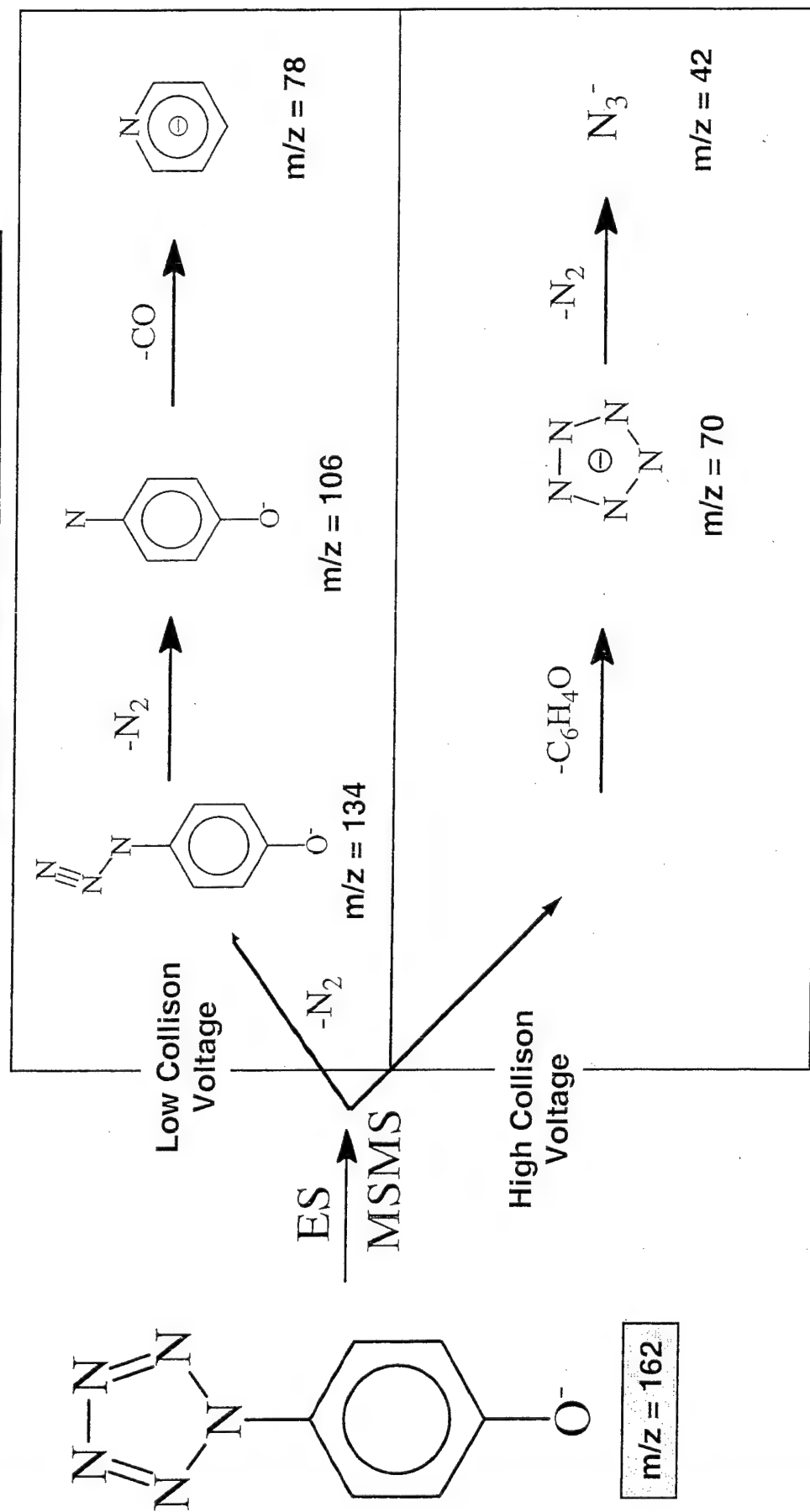




ESIMS of para-Phenoxypentazole

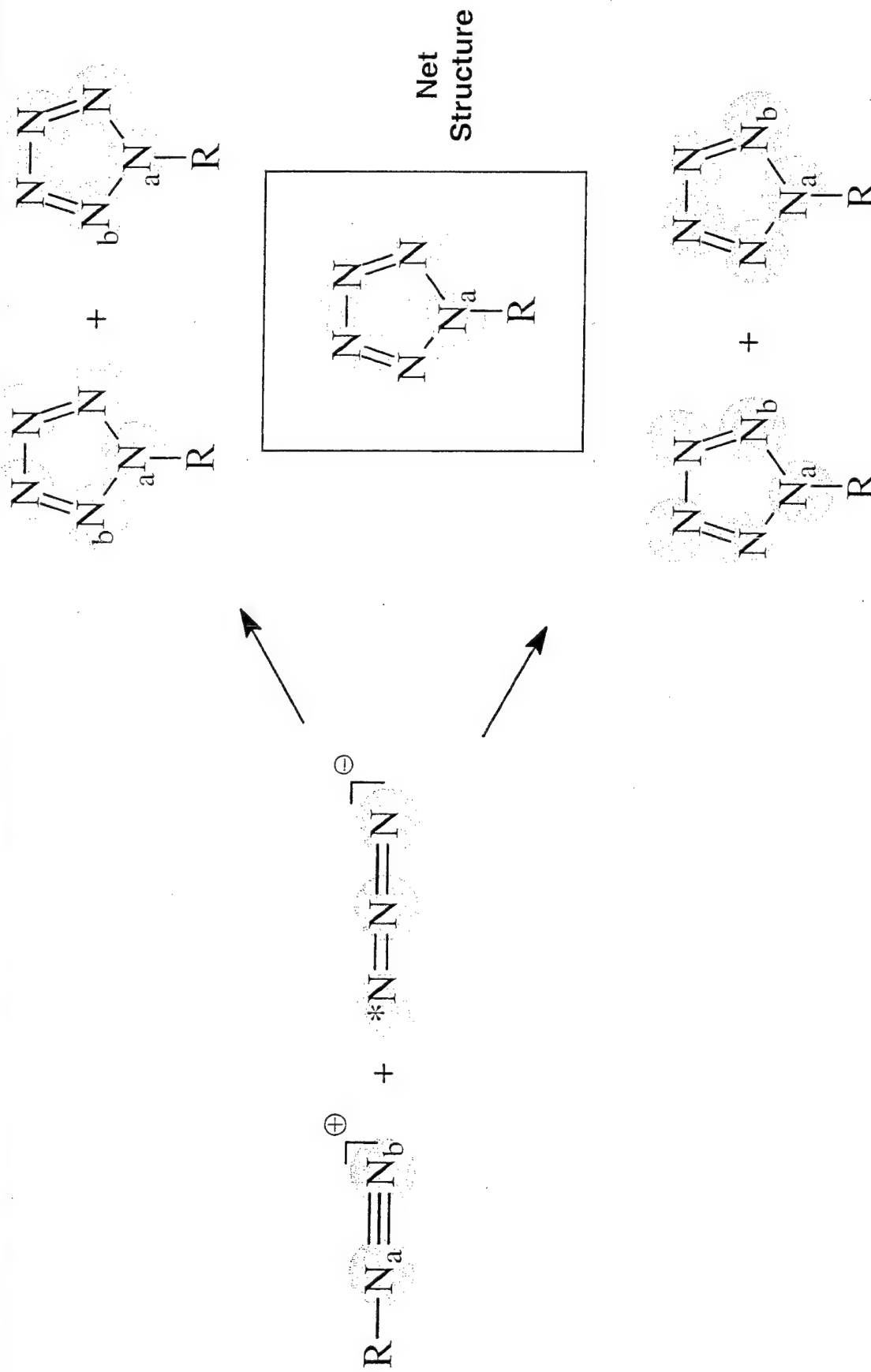


Observed peaks in the MSMS of 162





^{15}N Labeling of the Pentazole Ring

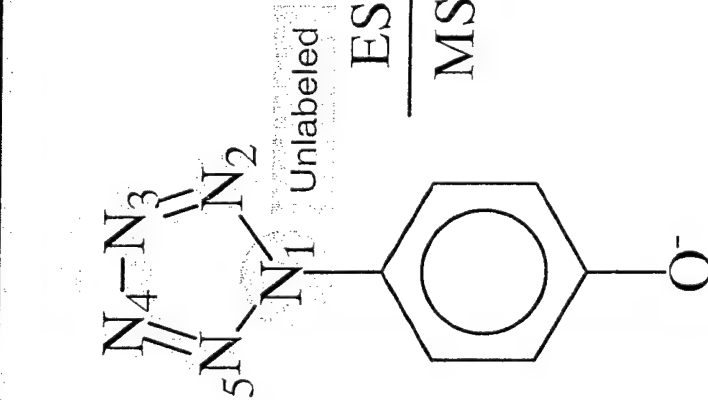




Is the Peak at m/e 70 indeed due to the Pentazole Anion???

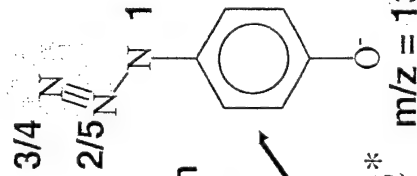


^{15}N Labeled Pentazole



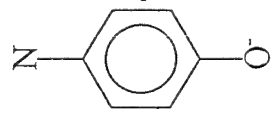
ES
MSMS

Low Collision
Voltage

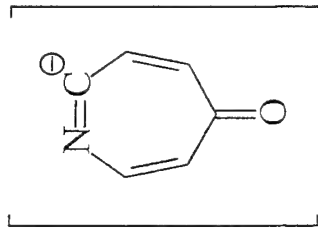


$-\text{N}_2^*$
or $-\text{N}_2$

$m/z = 135/134$

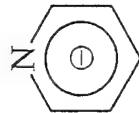


$m/z = 106$



$-\text{CO}$

$m/z = 78$



Labeling experiment shows that CO is
lost in the last step

High Collision
Voltage



$m/z = 71$

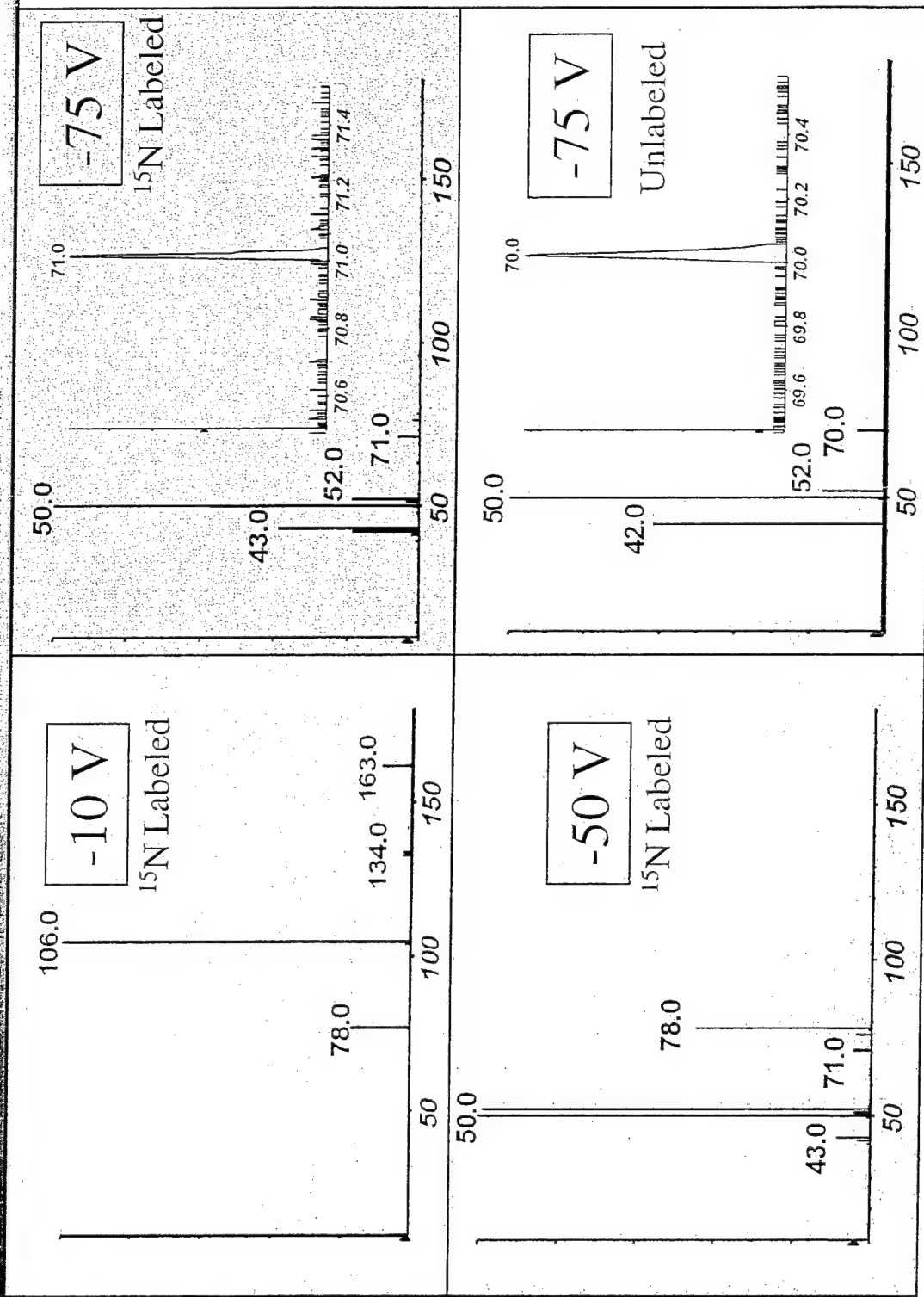
$m/z = 163$

^{15}N statistically distributed
over $\text{N}_2, \text{N}_3, \text{N}_4$ & N_5

Definitive proof for the pentazole anion



MSMS of the Parent Ion Peak

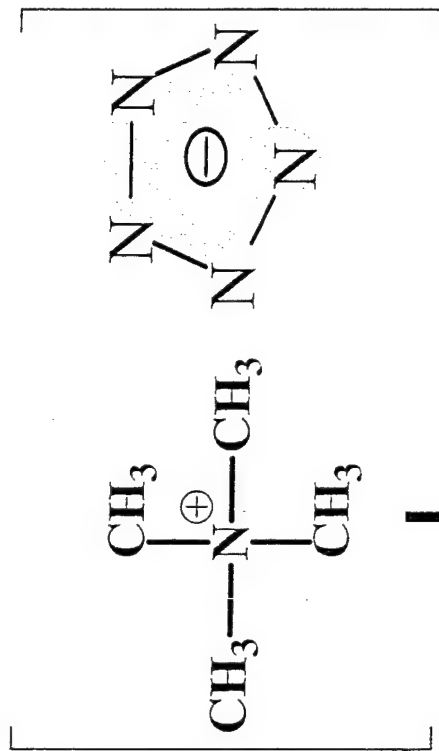
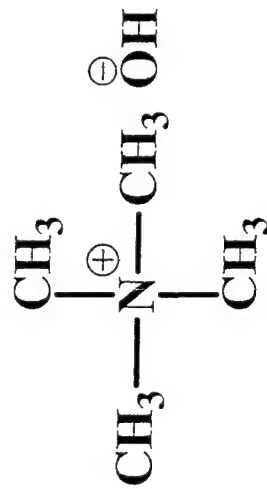
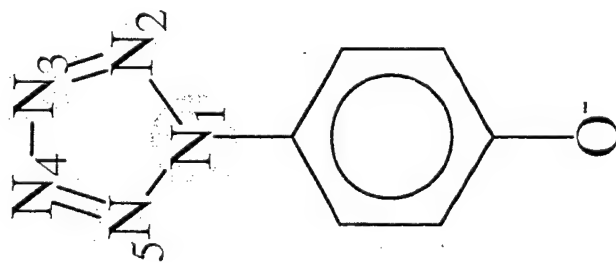


m/z

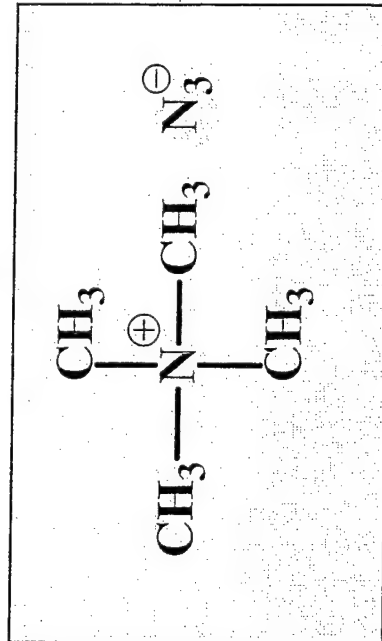
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Chemical Cleavage of the C-N Bond ?

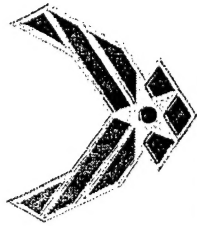


Not Isolated

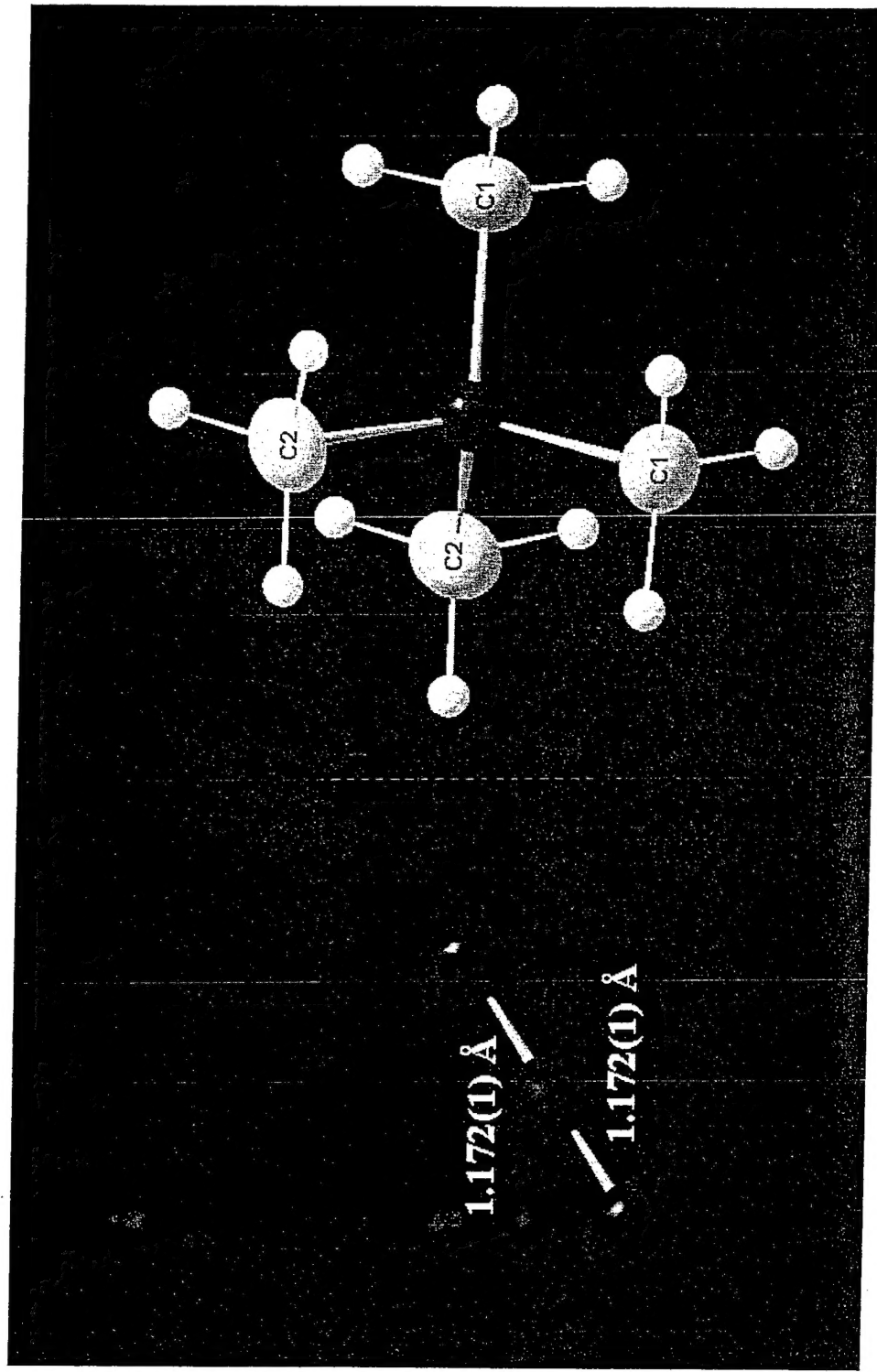


Formation of azide from decomposition of N_5^-

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Crystal Structure of Residue



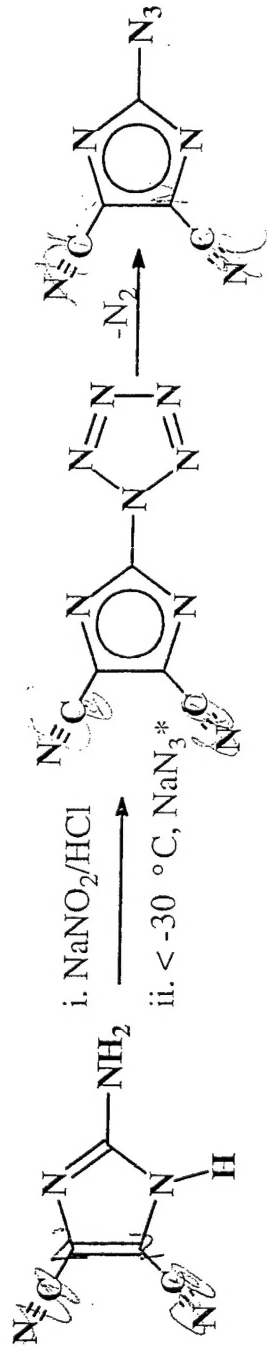
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Pentazoles with Heterocyclic Substituents

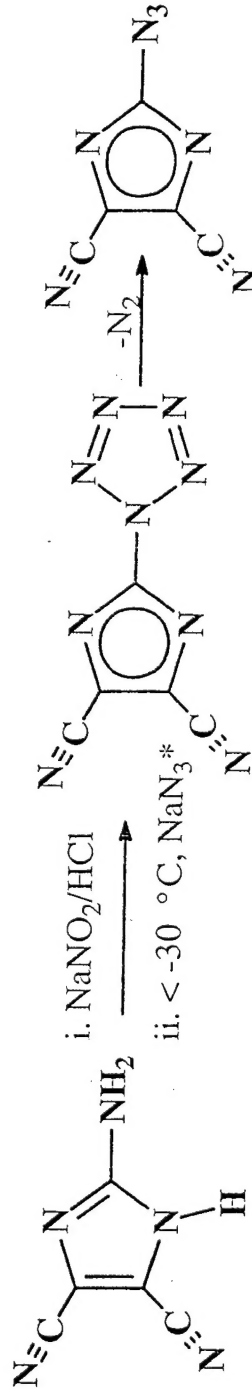


- These systems are unstable above -70 °C and the pentazole ring rapidly decomposes to liberate N₂ gas.



A. Hammerl and T. M. Klapoetke, *Inorg. Chem.* **2002**, 41, 906-912

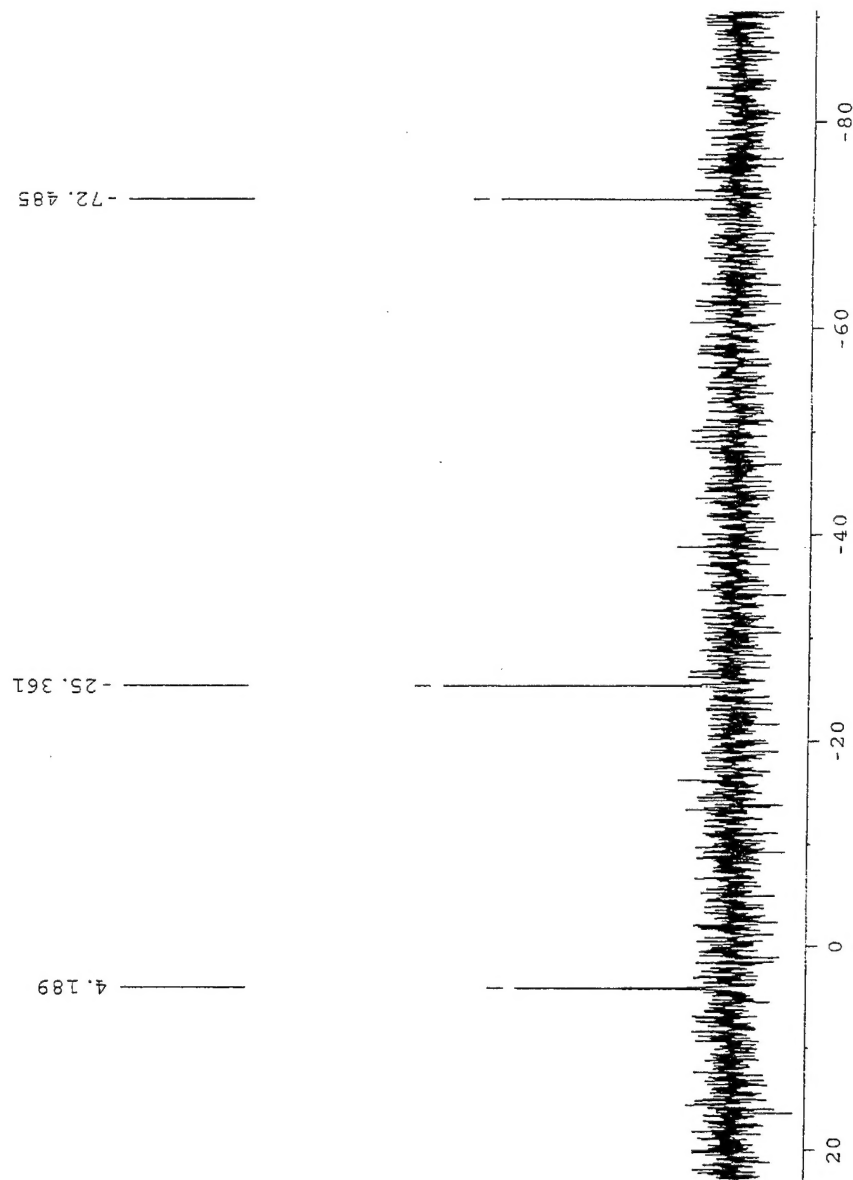
- Pentazole derived from 2-amino-4,5-dicyanoimidazole shows higher thermal stability



Christe Symposium, 225th National ACS Meeting, New Orleans, March 25-26, 2003



^{15}N NMR of 2-amino-4,5-dicyanoimidazolyl pentazole



^{15}N NMR recorded in a mixture of methanol and acetonitrile at $-30\text{ }^{\circ}\text{C}$, nitromethane used as an external reference (0 ppm)

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Summary



- Synthesized aryl pentazoles: hydroxy group at the *para*-position on the aryl ring gives the best results.
- Demonstrated selective cleavage of C-N bond by ESIMS with retention of pentazole ring. Results confirmed studying ^{15}N labeled pentazoles.
- First experimental detection of pentazole anion
- Synthesis of pentazoles with a heterocyclic substituents
- Offers potential pathway for bulk synthesis of N_5^- salts